# The Physical and Molecular Properties of New Low Melting Nematics with Negative Dielectric Anisotropy

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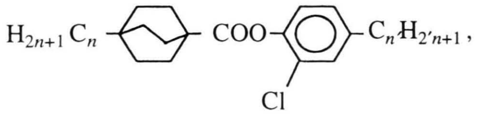
The paper presents some basic physical properties (static electric permittivities, refraction indices, density and viscosity) of 2-chloro-4-n′-alkylphenyl esters of 4-*n*-alkylbicyclo[2,2,2]octane-1-carboxylic acids ($n'=7$, $n=5$ and 7) which are, at room temperature, nematics with a negative dielectric anisotropy. On the basis of temperature dependence of the principal static permittivities $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$ of the nematics, using the Maier-Meier equations, the angle between the dipole moment vector and the long axis of mesogenic molecules, the apparent molecular dipole moment square $\mu^2_{\mathrm{app}}(T)$, and the nematic order parameter $S(T)$ were determined.

*Key words:* Nematics; Dielectric Anisotropy; Density; Viscosity.

## 1. Introduction

Stable nematic liquid crystals with a negative dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$) are used in some kind of displays [1–3] and as anisotropic solvents for spectroscopic investigations [4]. Among numerous hitherto synthesized compounds of this type only MBBA (*p*-metoxybenzylidene-*p*′-*n*-butylaniline) shows the nematic phase at room temperature (Cr 21° N 45° I). MBBA was the subject of an impressive number of publications [5], and the anisotropic properties of this compound are considered as representative for the whole class of nematics with negative $\Delta\varepsilon$. However, the published results often differ considerably, which may be caused by the thermal instability of MBBA and its chemical activity.

In this paper we present the physical properties of new low melting and stable nematics with negative dielectric anisotropy. These are 2-chloro-4-*n*′-alkylphenyl esters of 4-*n*-alkylbicyclo[2,2,2]octane-1-carboxylic acids with the chemical formula



($n'$CP$n$BOC). (I)

For the compounds with $n'=7$ and $n=5$ and 7, the following sequence of the phase transitions is observed:

7CP5BOC: Cr 18.2 °C N 43.5 °C I,
7CP7BOC: Cr 14.1 °C N 48.5 °C I.

Both compounds supercool quite easily down to about −30 °C.

## 2. Experimental

The method of the synthesis of $n'$CP$n$BOC's has been described in [6].

The static electric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured at 1 kHz with a Wayne-Kerr 6425 bridge. The liquid crystal sample was placed within a planar copper capacitor with gold covered electrodes. The distance between the electrodes was 0.6 mm. A magnetic field **B** of 0.6 T was used for the sample orientation in the nematic phase. The permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of the ordered nematic were measured with the electric field **E** parallel and perpendicular to **B**, respectively. The accuracy of the permittivity measurements was 0.1%, and the temperature was stabilized within 0.01 °C.

The refractive indices were measured by means of an appropriately prepared Abbe refractometer ($\lambda = 589$ nm). The accuracy of the measurements was $\pm 2 \cdot 10^{-4}$ for $n_0$ and $\pm 5 \cdot 10^{-4}$ for $n_e$.

The density measurements were carried out with an Anton Paar DMA 60/602 vibration tube densimeter with an accuracy of $5 \cdot 10^{-5}$ g/cm$^3$.

The viscosity was determined with a Haake viscometer Rotovisco RV20 with the measuring system CV100, the share rate being 275 s$^{-1}$. The measuring system consists of the rotary beaker filled with the liquid and the cy-

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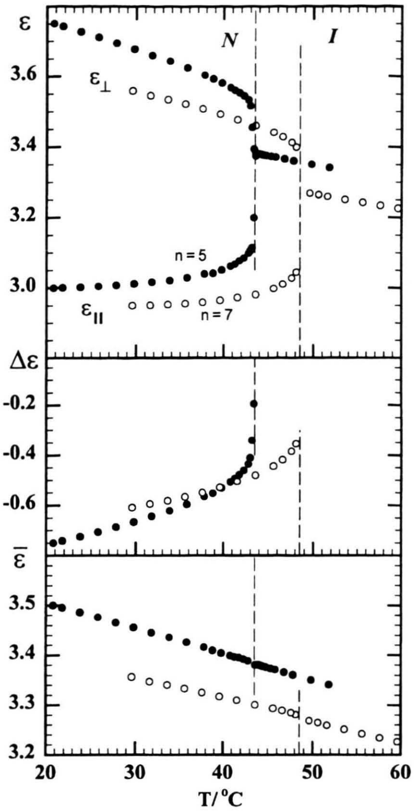

Fig. 1. Temperature dependence of the permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, and the mean permittivity $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\,\varepsilon_{\perp})/3$, for 7CP*n*BOC, $n=5$ and 7.

lindrical sensor of Mooney-Ewart type (ME15) placed in centre of the beaker. The liquid gap was 0.5 mm.

## 3. Results and Discussion

Figure 1 presents the temperature dependence of the principal permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, and the mean permittivity $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\,\varepsilon_{\perp})/3$ for 7CP*n*BOC, $n=5$ and 7. The compounds show a rather low polarity ($\bar{\varepsilon} \approx 3$), and at room temperature the dielectric anisotropy is about $-0.7$. At the isotropic to nematic phase transition temperature the mean value of the permittivity $\bar{\varepsilon}$ exhibits a very small positive jump.

Figure 2 shows the temperature dependences of the ordinary $n_0$ and extraordinary $n_e$ indices of refraction and the optical anisotropy $\Delta n = n_e - n_0$ for the studied compounds (I).

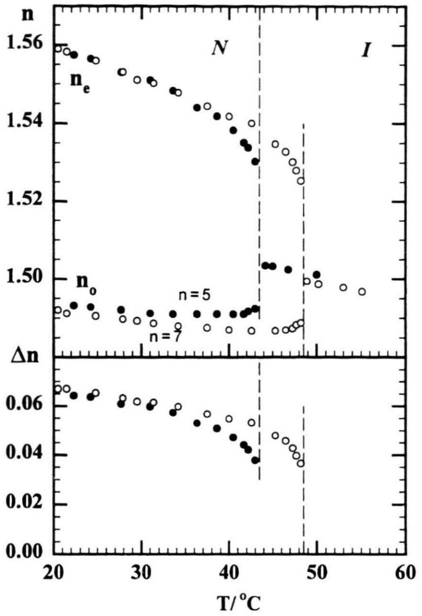

Fig. 2. Temperature dependence of the ordinary $n_0$ and extraordinary $n_e$ indices of refraction and optical anisotropy $\Delta n = n_e - n_0$, for 7CP*n*BOC, $n=5$ and 7.

Figure 3 presents the temperature dependence of the density and the molar volume of the compounds (I) in the isotropic and nematic phases. The molar volume jump at the nematic to isotropic phase transition temperature is about 1 cm$^3$/mol (~ 0.2%) for both studied compounds. The difference in the molar volume of 7CP7BOC and 7CP5BOC is about 33 cm$^3$/mol in the nematic phase and 34 cm$^3$/mol in the isotropic phase. The values are very close to the molar volume of the $-CH_2CH_2-$ group estimated from volumetric studies of *n*-alkylcyanobiphenyls [7].

Figure 4 shows the temperature dependence of the viscosity of the compounds (I). A sharp decrease of the viscosity is observed at the isotropic to nematic transition. It means that, as expected in the measuring method we used, the nematic flow leads to molecular ordering, and finally for the stationary flow the velocity gradient is perpendicular to the director **n**. In such a situation the nematic viscosity has the least possible value [5]. In terms of the Męsowicz coefficients [8] the nematic viscosity measured in our experiment is rather close to $\eta_2$. The viscosity activation energy resulting from the Arrhenius plot (Fig. 5) equals to 32 ± 1 kJ/mol in the isotropic and nematic phases of both studied compounds (I).

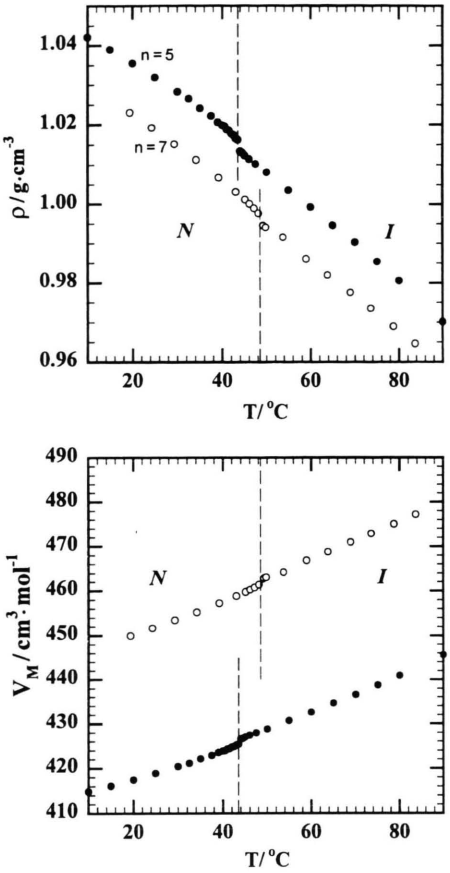

Fig. 3. The density and molar volume of 7CP*n*BOC, *n*=5 and 7, as a function of temperature.

### *Molecular Interpretation of the Static Dielectric Properties of 7CPnBOC's, n = 5 and 7*

From the experimental data of the static permittivities (Fig. 1) some important molecular quantities can be obtained using the Maier-Meier equations [9]

$$\varepsilon_{\parallel}(T) = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} + \frac{2}{3}\,\Delta\alpha \cdot S + F \cdot \frac{\mu_{\mathrm{app}}^2}{3\,kT} \cdot [1 - (1 - 3\cos^2\beta)\,S]\right\},$$

$$\varepsilon_{\perp}(T) = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} - \frac{1}{3}\,\Delta\alpha \cdot S + F \cdot \frac{\mu_{\mathrm{app}}^2}{3\,kT} \cdot \left[1 + \frac{1}{2}(1 - 3\cos^2\beta)\,S\right]\right\}, \tag{1}$$

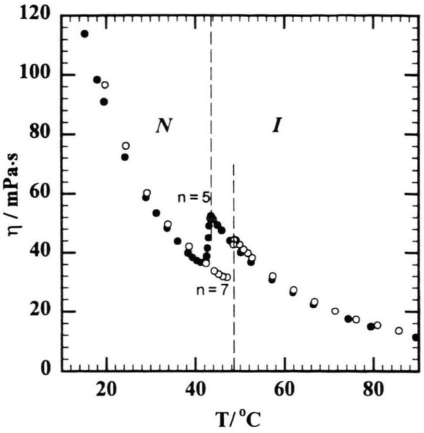

Fig. 4. The viscosity of the isotropic and nematic phases of 7CP*n*BOC, *n*=5 and 7, as a function of temperature.

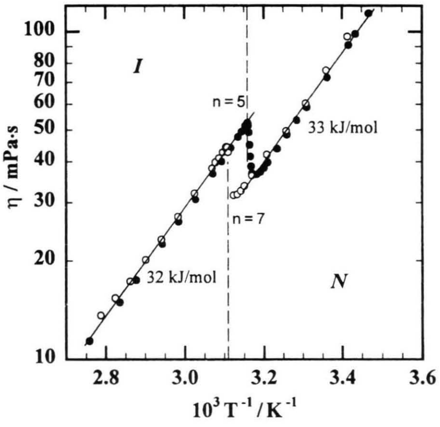

Fig. 5. Arrhenius plots for the viscosity of 7CP*n*BOC, *n*=5 and 7.

where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m, $N$ is the number of molecules per unit volume, $\mu_{\mathrm{app}}$ the molecular apparent dipole moment, and $h$ and $F$ are Onsager local field factors:

$$h = \frac{3\,\bar{\varepsilon}}{2\,\bar{\varepsilon} + 1}, \quad F = \frac{1}{1 - \bar{\alpha}\,f}, \quad f = \frac{2\,(\bar{\varepsilon} - 1)}{2\,\bar{\varepsilon} + 1}\,\frac{N}{3\,\varepsilon_0}. \tag{2}$$

$\bar{\alpha}$ and $\bar{\varepsilon}$ are the mean values of the polarizability and the permittivity, respectively:

$$\bar{\alpha} = \frac{1}{3}(\alpha_{\mathrm{l}} + 2\,\alpha_{\mathrm{t}}), \quad \bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\,\varepsilon_{\perp}), \tag{3}$$

and

$$\Delta\alpha = \alpha_{\mathrm{l}} - \alpha_{\mathrm{t}} \tag{4}$$

denotes the anisotropy of the polarizability. $\alpha_l$ and $\alpha_t$ are the composants of the polarizability tensor along the

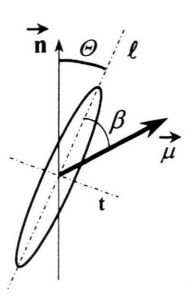

Fig. 6. Geometrical quantities describing a dipolar nematogenic molecule situated inside the oriented nematic sample. The vector $\mu$ denotes the resulting dipole moment of the molecule, and **n** is the direction of the nematic macroscopic orientation. l and t represent the molecular long and short axes, respectively.

long (l) and short (t) molecular axis, respectively (see Figure 6). $\beta$ is the angle between the total dipole moment vector $\mu$ of the nematogen molecule and its long axis. $S$ is the order parameter defined as

$$S=\frac{1}{2}\left\langle 3\cos^2\Theta-1\right\rangle, \tag{5}$$

where $\Theta$ is the angle between the molecular long axis and the direction of the macroscopic orientation indicated by **n** (see Figure 6).

For the isotropic phase ($\varepsilon_{\parallel}=\varepsilon_{\perp}=\varepsilon, S=0$), equations (1) transform into the Onsager equation [10]

$$\frac{(\varepsilon-n^2)(2\,\varepsilon+n^2)}{\varepsilon\,(n^2+2)^2}=\frac{N}{3\,\varepsilon_0}\,\frac{\mu_{\text{app}}^2}{3\,kT}, \tag{6}$$

where the refraction index $n$ and the polarizability $\alpha$ are connected by the Lorenz equation

$$\frac{n^2-1}{n^2+2}=\frac{N}{3\,\varepsilon_0}\,\alpha\,. \tag{7}$$

From the molecular physics point of view, the significance of the static dielectric measurements of the oriented nematic samples consists mainly in the possibility of determining, with use of (1), the angle $\beta$ between the vector of the dipole moment of the mesogenic molecule and its long axis. There are no other methods for determining that angle for molecules in the liquid state. It was shown in [11] that the values of $\mu_{\text{app}}^2$ and $\beta$, resulting from the fitting of the theoretical dependences $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$, given by (1), to the experimental values, strongly depend on the chosen function of the temperature dependence of the nematic order parameter $S\,(T)$. Particularly sensible to the $S\,(T)$ dependence is the apparent dipole moment $\mu_{\text{app}}^2\,(T)$.

In principle, the $S\,(T)$ dependence can be derived from measurements of any anisotropic property of the nematic, for example, the refractive index $\Delta n$, magnetic susceptibility $\Delta\chi$ or spectroscopic (Raman, NMR) absorption [12]. In general, the $S\,(T)$ function taken from an experiment leads to a situation where the $\mu_{\text{app}}^2\,(T)$ function resulting from the best fitting of the parallel component of the permittivity $\varepsilon_{\parallel}(T)$ is quite different from the $\mu_{\text{app}}^2$ $(T)$ function corresponding to the fitting of the perpendicular component $\varepsilon_{\perp}(T)$ [11]. Sometimes such a result is interpreted as an anisotropy in the dipole-dipole interaction, but in fact the result has no physical meaning because in the both equations (1) $\mu_{\text{app}}^2$ must be the same quantity.

For the above reason we have proposed [11] a new way of the interpretation of the static dielectric properties of nematics with use of the Maier-Meier equations (1). Namely, the fitting of the theoretical dependences $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$ to the experimental data should be performed with an additional condition of the identity of the $\mu_{\text{app}}^2\,(T)$ for both components of the permittivity. Then, due to that self-evident requirement, the fitting provides quite accurate and univocal values of $\mu_{\text{app}}^2\,(T)$, the angle $\beta$ and the order parameter $S\,(T)$. The fitting procedure becomes markedly simplified when the $S(T)$ dependence is expressed in the empirical form [13]

$$S(T)=\left(1-\frac{T}{T_{\text{NI}}}\right)^{z}, \tag{8}$$

where $T_{\text{NI}}$ denotes the nematic to isotropic phase transition temperature (in K). It is a very useful expression, since for different nematics (different $T_{\text{NI}}$), the function $S\,(T)$ is determined by one parameter ($z$) only.

The mean polarizability $\bar{\alpha}$ and the anisotropy of polarizability $\Delta\alpha$ have been calculated from the optical measurements: $\bar{\alpha}=50.2\cdot10^{-24}\,\text{cm}^3$, $\Delta\alpha=11.0\cdot10^{-24}\,\text{cm}^3$ for 7CP5BOC, and $\bar{\alpha}=53.8\cdot10^{-24}\,\text{cm}^3$, $\Delta\alpha=10.1\cdot10^{-24}\,\text{cm}^3$ for 7CP7BOC.

In Figs. 7(a) and 8(a) the solid lines present the best fitting of the theoretical dependences given by the Maier-Meier equations (1), to the experimental data. The fitting fulfils the condition of coincidence of $\mu_{\text{app}}^2\,(T)$, as shown in Figs. 7(b) and 8(b). In part (c) of the figures the solid lines represent the $S\,(T)$ dependence corresponding to the $z$ value resulting from the fitting. For both studied compounds the obtained $S\,(T)$ function is very close to that derived from the optical anisotropy measurements. The angle $\beta$ for both nematogen molecules equals to about 80°, what is in accordance with our expectation in view

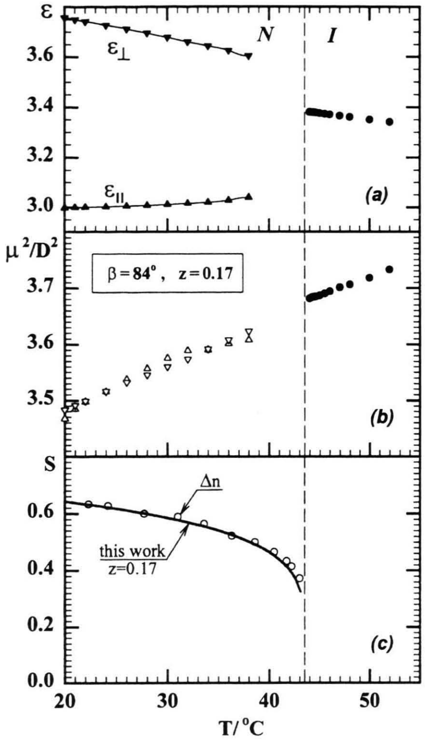

Fig. 7. The solid lines in (a) represent the best fitting of the theoretical dependences (1) to the experimental data (points) for 7CP5BOC with the condition of coincidence of $\mu^2_{\text{app}}(T)$ (b). In (c) the obtained $S(T)$ dependence is compared with that resulting from the $\Delta n$ measurements.

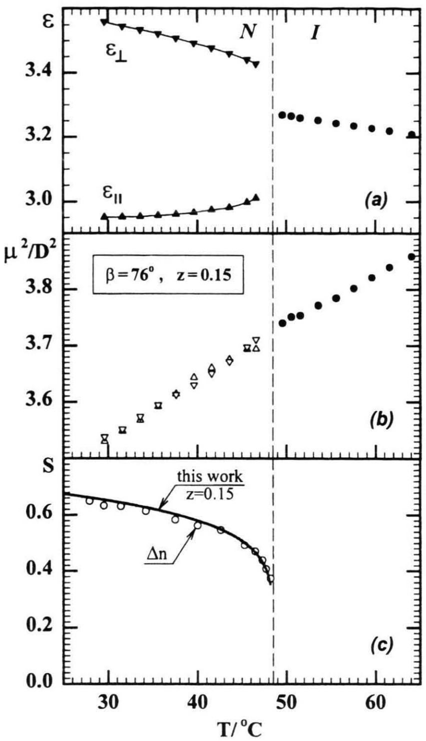

Fig. 8. The best fitting (a) of (1) (solid lines) to the experimental data (points) for 7CP7BOC was performed with the condition of coincidence of $\mu^2_{\text{app}}(T)$ (b). In (c) the $S(T)$ dependence is compared with that resulting from the $\Delta n$ measurements.

of the structure of 7CP*n*BOC with a dipolar substituent (–Cl) in a lateral position.

The results presented in Figs. 7 (a) and 8 (a) show that, due to the imperfect molecular ordering close to the nematic to isotropic transition, these results cannot be interpreted in the frame of the Maier-Meier equations, i.e. with the same $\beta$, $S(T)$ and $\mu^2_{\text{app}}(T)$ both for $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$. Probably the molecular orientation forced by the magnetic field is strongly disturbed by the nematic – electrode surface interactions in the vicinity of the phase transition. The effect is very distinct for 7CP5BOC, where the static dielectric properties obey the Maier-Meier predictions only at about five degrees below the $T_{\text{NI}}$.

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